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Field of the invention

The invention relates to kollagenfreie cosmetic preparing, which one receives by crosslinking from cationic biopolymers with polyols and diisocyanates and/or dialdehydes, as well as a method to their preparation.

State of the art

Cosmetic fleeces become used as humidity masks for face and hands. Usually these preparing on basis of animal collagen become prepared, by adjusting aqueous Kollagensuspensionen to a pH value in the acidic range and subsequent by freezing drying process dewatered. In trains of the continuous criticism at animal products an increasing need exists after products in the market, which become exclusive prepared using vegetable or marine raw materials.

From the Japanese patent application JP-A2 Hei 6/048 917 is beauty packings with chitosan as active component as well as organic acidic one and collagen as other ingredients known. Subject-matter of the Japanese patent application JP-A2 Hei 4/275 207 are humidity-binding additions to strike-cosmetic agents, with which it acts around powdery mixtures of chitosan and collagen. In JP-A Hei 1/066204 becomes a method the preparation of colored Chitosanpartikel described, with which one aqueous cross-linking products of chitosan with diisocyanates, diepoxides or dicarbonic acid halides into an hot gas phase sprayed.

The object of the invention consisted thus of making strike-cosmetic agents available on the one hand free of animal collagen is and on the other hand to the preparation of humidity masks for face and hands is suitable.

Description of the invention

Subject-matter of the invention are kollagenfreie cosmetic preparing, which one receives, by one poured, aqueous suspensions of cationic biopolymers with (A) polyols and (B) diisocyanates and/or dialdehydes crosslinked and subsequent dewatered.

Surprisingly it was found that with the cationic biopolymers of water-insoluble, but very good, elastic fiber networks prepared wettable with water to become to be able, which correspond to the known Kollagenschwämmen in their properties. The invention includes the finding that with others in principle in considerations coming starting materials, as for example vegetable proteins or fiber-formed biopolymers (z. B. Cellulose, pectin) only products obtained become, which prove in the application as brittle or dissolve in waters.

An other subject-matter of the invention relates to a method to the preparation of kollagenfreien cosmetic preparing, with which one poured, aqueous suspensions of cationic biopolymers with (A) polyols and (B) diisocyanates and/or dialdehydes staggered and subsequent dewatered.

Cationic biopolymers

Cationic biopolymers, like z. B. Chitosans, become the group of the hydraulic colloids counted. Chemical considered concerns it partial deacetylierte chitins of different molecular weight, which contain the subsequent - idealized - monomer component:

EMI2.1

Contrary to most hydraulic colloids, which are in the range of biological pH values negatively charged, chitosans represent bottom these conditions of cationic biopolymers. Those positive loaded chitosans can step and become with opposite charged surfaces into interaction therefore into cosmetic hair and toiletries as well as pharmaceutical preparing used (see. Ullmann's Encyclopedia OF Industrial Chemistry, 5th OD., volume. A6, Weinheim, publishing house chemistry, 1986, S. 231-332). Reeves to this subject are also for example from B. Gesslein et al. in HAPPI 27, 57 (1990), O. Skaugrud in Drug Cosm. Ind. 148, 24 (1991) and E. Onsoyev et al. into soap oil fat wax 117, 633 (1991) appeared.

To the preparation of the chitosans one proceeds with chitin, preferably the bowl remainders from crustaceans, which as inexpensive raw materials in large amounts for the order. The chitin becomes thereby in a method for the first time of chopping man et al. described is, usually first by addition of bases deproteiniert, by addition by mineral acids demineralized and finally by addition of strong bases deacetyliert, whereby the molecular weights can be distributed over a broad spectrum. Corresponding methods are for example from macro mol. Chem. one. 177, 3589 (1976) or the French

patent application FR-A 27 01266 known.

Crosslinking agent

As crosslinking agents (A) polyols and (B) of diisocyanates and/or dialdehydes used become. Diisocyanates, which come to the crosslinking of the cationic biopolymers into considerations, preferably follow the formula (I),
 $O=CN[X]-NC=O$ (I)
 in the X for a linear or branched, naphthenischen or aromatic hydrocarbon radical with 1 to 12 carbon atoms stands. Preferably hexamethylene diisocyanate becomes used as crosslinking agents. As dialdehydes fabrics come into considerations, which follow the formula (II),
 $OHC[Y]-CHO$ (II)
 in Y for a linear or branched, naphthenischen or aromatic hydrocarbon radical with 1 to 12 carbon atoms stands. Preferably Glutardialdehyd becomes used as crosslinking agents.

The crosslinking agents (B) can do in amounts from 0,5 to 10, preferably 1 to 8 and in particular 2 to 5 Gew. - % - related to the dry substance of the cationic biopolymers - used become.

Polyols

Polyols, which become as crosslinking agents (A) used, preferably possess 2 to 15 carbon atoms and at least two hydroxyl groups. Typical examples are:

- Glycerol;
- Alkylenglycole as for example ethylene glycols, diethylene glycols, propylene glycols, butylene glycols, Hexylenglycol as well as Polyethylenglycole with an average molecular weight of 100 to 1,000 Dalton;
- technical Oligoglyceringemi with an own condensation degree from 1,5 to 10 as for instance technical Diglyceringemi with a Diglyceringehalt from 40 to 50 Gew. - %;
- Methylvverbindungen, like in particular trimethylethane, trimethylpropane, Trimethylbutan, pentaerythritol and dipentaerythritol;
- Niedrigalkylglucoside, in particular such, with 1 to 6 carbons in the alkyl radical as for example methyl and Butylglucosid;
- Sugar alcohols with 5 to 12 carbon atoms as for example sorbitol or mannitol,
- Sugar with 5 to 12 carbon atoms as for example glucose or sucrose;
- Aminozucker as for example Glucamin.

Usually the polyols (A) in amounts from 0,1 to 10 become, preferably 2 to 8 Gew. - % - related to the dry substance of the chitosan used, whereby the use of glycerol and Polyethylenglycolen preferred is.

Preparation of the preparing

Usually aqueous solutions become and/or. Suspensions of the cationic biopolymers, preferably chitosan, with a dry matter content from 0,5 to 3, preferably 1,8 to 2,2 Gew. - % at a pH value from 3,5 to 6,0, preferably 5,0 to 5,7 by addition of inorganic or organic acidic ones, preferably hydrochloric acid, prepared, whereby the temperature should become so selected that it the swelling that biopolymers assisted. Usually this preferably lies within the range of 20 to 50 and 35 to 45 DEG C. In this way prepared suspensions contain undissolved particles also poured beside the solved biopolymers. Mentioned the viscosity of the suspension adjusted by the conditions can affect the later mechanical properties of the fleeces. The maintenance of the elasticity in the dried state the suspensions then polyols become (A) and other cosmetic ingredients added. For the mechanical properties of the fleeces it proved in addition as favourable, to the suspensions natural fibers, as for example lignin, Polyose, pectin and in particular cellulose, or however synthetic fibers as for example polyesters, polyamides or their mixtures in an amount from 1 to 50, preferably 5 to 10 Gew. - to add %. It is particularly recommendable to in addition-admit the fibers before the homogenization of the solution. Subsequent ones become the suspensions homogenized, with the diisocyanates and/or dialdehydes crosslinked and dewatered.

Auxiliary and additives

The preparing according to invention can contain compatible surfactants in subordinate amounts with the other ingredients. Typical examples are Fettalkoholpolyglycolethersulfate, Monoglyceridsulfate, mono and/or Dialkylsulfosuccinate, Fettsäureisethionate, Fettsäuresarcosinate, Fettsäuretauride, Ethercarbonsäuren, Alkylglykogluoside, Fettsäureglucamide, Alkylamidobetaine and/or preferably vegetable protein fatty acid condensates.

Furthermore they can contain oil bodies, emulsifiers, over greasing means, stabilisers, wax, consistency givers, thickeners, cation polymers, silicone compounds, biogenous active ingredients, film formers, preservatives, Hydrotrope, Solubilisatoren, UV adsorbers, color and fragrances and such a thing as other auxiliary and additives.

As oil bodies for example Guerbetalkohole come on basis of fatty alcohols with 6 to 18, preferably 8 to 10 carbon atoms, esters of linear C6-C20-Fettsäuren with linear C6-C20 fatty alcohols, esters of branched C6-C13-Carbonsäuren with linear C6-C20-Fettalkoholen, ester of linear C6-C18-Fettsäuren with branched alcohols, in particular 2-Ethylhexanol, ester of linear and/or branched fatty acids with multi-valued alcohols (like z. B. Dimerdiol or Trimertriol) and/or Guerbetalkoholen, triglycerides on basis C6-C10-Fettsäuren, ester of C6-C22-Fettalkoholen and/or Guerbetalkoholen with aromatic carbonic acids, in particular benzoic acid, vegetable oils, branched primary alcohols, substituted cyclohexanes, Guerbetcarbonate, Dialkylether, silicone oils and/or aliphatic and/or. naphthenische hydrocarbons in considerations.

As emulsifiers for example nichtionogene surfactants come from at least one of the subsequent groups into question:

1. Accumulation products from 2 to 30 mole ethylene oxide and/or 0 to 5 mole propylene oxide to linear fatty alcohols with 8 to 22 C-atoms, at fatty acids with 12 to 22 C-atoms and to alkyl phenols with 8 to 15 C-atoms in the alkyl group;
2. C12/18-Fettsäuremono- und - more diester of accumulation products of 1 to 30 mole ethylene oxide at glycerol;
3. Glycerinmono- und - more diester and Sorbitanmono- und - more diester of saturated and unsaturated fatty acids with 6 to 22 carbon atoms and their products of accumulation of ethyl oxide;
4. Alkyl mono- und - oligoglycoside with 8 to 22 carbon atoms in the alkyl radical and their ethoxylated analogues;
5. Accumulation products Ricinusöl hardened from 15 to 60 mole ethylene oxide to Ricinusöl and/or;
6. Polyole and in particular Polyglycerinester such as z. B. Polyglycerinpolyricinoleat or Polyglycerinpoly-12-hydroxystearat. Likewise suitable is mixtures of compounds from several these substance classes;
7. Accumulation products Ricinusöl hardened from 2 to 15 mole ethylene oxide to Ricinusöl and/or;
8. Partial ester on basis linear, more branched, more unsaturated and/or. satisfied C12/22-Fettsäuren, Ricinolsäure as well as 12-Hydroxystearinsäure und glycerol, polyglycerol, pentaerythritol, dipentaerythritol, sugar alcohols (z. B. Sorbitol) as well as Polyglycoside (z. B. Cellulose);
9. Tri alkyl phosphates;
10. Wollwachsalkohole;
11. Polysiloxan polyalkyl polyethercopolymers and/or. corresponding derivatives;
12. Mixing ester from pentaerythritol, fatty acids, citric acid and fatty alcohol in accordance with DE-PS 11 65 574 and/or mixing esters of fatty acids with 6 to 22 carbon atoms, methyl glucose and polyols, preferably glycerol as well as
13. Polyalkylenglycole.

The accumulation products of ethylene oxide and/or of propylene oxide to fatty alcohols, fatty acids, alkyl phenols, Glycerinmono- und - more diester as well as Sorbitanmono- und - more diester of fatty acids or at Ricinusöl represent known, in the trade available products. It acts itself thereby around homologous mixtures, whose middle Alkoxylierungsgrad corresponds to the ratio of the amounts of material of ethylene oxide and/or propylene oxide and substrate, becomes performed with which the addition reaction. C12/18-Fettsäuremono- und - of accumulation products of ethylene oxide at glycerol 20 24 051 than back greasing means for cosmetic preparation known are more diester from DE-PS.

C8/18-Alkylmono- und - oligoglycoside, their preparation and their use as surface-active fabrics are for example from US 3.839.318, US 3.707.535, US 3.547.828, DE-OS 19 43 689, DE-OS 20 36 472 and DE 30 01 064 A1 as well as EP 0,077,167 A1 known. Its preparation made in particular by conversion of glucose or oligosaccharides with primary alcohols with 8 to 18 C-atoms. Concerning glycoside remainder applies that both mono glycosides, bound with which a cyclic sugar residue is glycosidisch to the fatty alcohol and oligomere glycosides with a Oligomerisationsgrad to preferably about 8 suitable are. The Oligomerisationsgrad is thereby a statistical average, for which an homologous distribution conventional for such technical products is the basis.

Further zwitterionic surfactants can become used as emulsifiers. As zwitterionic surfactants such surface-active compounds referred become, these in the molecule at least a quaternary ammonium group and at least one carboxylate and a sulfonate group inertial. Particularly suitable zwitterionic surfactants are the so called betaines like the N-alkyl-n, n dimethylammoniumglycinate, for example the Kokosalkyldimethylammoniumglycinat, N-Acylaminopropyl-n, N-dimethylammoniumglycinate, for example the Kokosacylamino-propyldimethylammoniumglycinat, and 2-Alkyl-3-carboxymethyl-3-hydroxyethylimidazoline with in each case 8 to 18 C-atoms in the alkyl or acyl group as well as the Kokosacylaminoethylhydroxyethylcarboxymethylglycinat. Particularly preferred is that the bottom CTA designation Cocamidopropyl of betaines known fatty acid amide derivative. Likewise suitable emulsifiers are ampholytic surfactants. Bottom ampholytic surfactants become such surface-active compounds understood, which except a C8/18-Alkyl- or - acyl group in the molecule at least a free amino group and at least a one - a COOH- or - SO₃H group contained and to the formation of inner salts capable is. Examples for suitable ampholytic surfactants are N-Alkylglycine, N-Alkylpropionsäuren, N-Alkylaminobuttersäuren, N-Alkyliminopropionsäuren, N-Hydroxyethyl-N-Alkylamidopropylglycine, N-Alkyltaurine, N-Alkylsarcosine, 2-Alkylaminopropionsäuren und Alkylaminoessigsäuren with about in each case 8 to 18 C-atoms in the alkyl group. Particularly preferred ampholytic surfactants are the N-Kokosalkylaminopropionat, the Kokosacylaminoethylaminopropionat und the C12/18-Acylsarcosin. Beside the ampholytic also quaternary emulsifiers come into considerations, whereby such are of the type of the Esterquats, preferably methylquaternierte Diätersäuretriethanolaminester salts, particularly preferred.

As over greasing means substances can become as for example lanolin and lecithin as well as polyethoxylated or acylated lanolin und Lecithinderivate, polyole fatty acid ester, monoglycerides und Fettsäurealkanolamide used, whereby the latter simultaneous serve as foam stabilisers. As consistency givers mainly fatty alcohols with 12 to 22 and preferably 16 to 18 carbon atoms and besides Partialglyceride come into considerations. Preferred one is a combination of these fabrics with Alkylglygoglycosiden und/or fatty acid N-methylglycididen same chain length and/or Polyglycerinpoly-12-hydroxystearaten. Suitable thickeners are for example polysaccharides, in particular Xanthan Gum, Guar gum, agar agars, alginates und Tylosen, carboxymethyl cellulose und carboxyethyl cellulose, furthermore high-molecular Polyethylenglycolmono- und - more diester from fatty acids, polyacrylates, polyvinyl alcohol und polyvinylpyrrolidone, surfactants as for example ethoxylated Fettsäureglyceride, ester of fatty acids with polyols as for example pentaerythritol or trimethylolpropane, Fettalkoholethoxylylate with concentrated homologous distribution or Alkylglygoglycoside as well as electrolytes such as common salt and ammonium chloride.

Suitable cationic polymers are for example cationic cellulose derivatives, cationic starch, copolymers of Diallylammoniumsalzen und acrylamides, quaternierte Vinylpyrrolidon/vinylimidazol polymers such as z. B. Luviquat TM, condensation products of Polyglycolen und amines, quaternierte Kollagenpolypeptide as for example Lauryldimmonium hydroxypropyl hydrolyzed collagen (Lamequat TM L), quaternierte Weizenpolypeptide, polyethylenimine, cationic silicone polymers such as z. B. Amidomethicone, copolymers of the adipic acid und Dimethylaminohydroxypropyldiethylentrimamin (Cartaretine TM), Polyaminopolyamide such as z. B. described in the FR-A 22 52 840 as well as their crosslinked water-soluble polymers, cationic Chitinderivate as for example quaterniertes chitosan, if necessary microcrystalline distributed, condensation products from Dihaloalkenalkylen such as z. B. Thiel Rome butane with until dialkyl amines such as z. B. Bis-Dimethylamino-1,3-propan, cationic Guar Gum such as z. B. Jaguar TM CBS, jaguar TM C-17, jaguar TM C-16, quaternierte ammonium salt of polymers such as z. B. Mirapol TM A-15, Mirapol TM AD-1, Mirapol TM AZ-1.

Suitable silicone compounds are for example dimethylpolysiloxanes, methyl phenylpolysiloxane, cyclic silicones as well as revision modification NO, fatty acid, alcohol, polyether, epoxy, fluorine and/or alkyl-modified silicone compounds, which can be present with room temperature both liquid and resinous. Typical examples for fats are Glyceride, as wax come and. A. Beeswax, paraffin wax or Mikrowachse if necessary in combination with hydrophilic wax, z. B. Cetylstearylalkohol or Partialglyceriden in question. As stabilisers metal salts of fatty acids can such as z. B. Magnesium, aluminum and/or zinc stearate used become. Bottom biogenous active ingredients are for example Bisabolol, Allantoin, Phytantriol, Panthenol, AHA acidic one, to understand plant extracts and Vitaminkomplexe. Film formers are for example chitosan, microcrystalline chitosan, quaterniertes chitosan, polyvinylpyrrolidone, Vinylpyrrolidon vinyl acetatecopolymers, polymers of the acrylic acid row, quaternary cellulose derivatives, collagen, hyaluronic acid and/or. their salts and similar compounds. Furthermore the improvement of the flow behavior Hydrotrope can become as for example ethanol, isopropyl alcohol, propylene glycols or glucose used. As preservatives are suitable for example phenoxyethanol, formaldehyde solution, Parabene, pentanediols or sorbic acid. As dyes the substances used approved suitable for cosmetic purposes and can become, like them for example in the publication "cosmetic coloring means" of the coloring material commission of the German research council, publishing house chemistry, Weinheim, 1984, S. 81-106 assembled are. These dyes become usually in concentrations from 0,001 to 0.1 Gew. - %, related to the entire mixture, used.

The total proportion of the auxiliary and additives can do 0.1 to 10, preferably 0, 5 to 5 Gew. - % - related to the dry substance cationic biopolymers - amount to. The agents can become the suspensions added, it are however likewise possible to moisten the finished masques before or during the application with these fabrics.

Example 1

In a 2-l-Rührapparat 1960 became ml water presented and on 40 DEG C heated and with 40 g chitosan (Hydagen TM CMFP) staggered. The pH value of the mixture became by addition of hydrochloric acid on 5,5 adjusted. Subsequent ones became 2 g (5 Gew. - % related to dry substance) glycerol added and the mixture in the Ultraturax homogenized. Afterwards 0.8 g (2 Gew became. - % related to dry substance) hexamethylene diisocyanate careful bottom-agitated. After the crosslinking the suspension was frozen as block and subsequent lyophilized. By columns of the dewatered block on the desired thickness elastic, water-insoluble fleeces became obtained, which behaved when dampening such as sponges.

Example 2

In a 2-l-Rührapparat 1960 became ml water presented and on 40 DEG C heated and with 40 g chitosan (Hydagen TM CMFP) staggered. The pH value of the mixture became by addition of hydrochloric acid on 5, 5 adjusted. Subsequent ones became 2 g (5 Gew. - % related to dry substance) glycerol and 2 g (5 Gew. - % related to dry substance) cellulose fibers added and the mixture in the Ultraturax homogenized. Afterwards 0.8 g (2 Gew became. - % related to dry substance) hexamethylene diisocyanate careful bottom-agitated. After the crosslinking the suspension was frozen as block and subsequent lyophilized. By columns of the dewatered block on the desired thickness elastic, water-insoluble fleeces became obtained, which behaved when dampening such as sponges.